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Published in:
Biochemical Systematics and Ecology

Link to article, DOI:
[10.1016/j.bse.2012.03.004](https://doi.org/10.1016/j.bse.2012.03.004)

Publication date:
2012

Document Version
Early version, also known as pre-print

[Link back to DTU Orbit](#)

Citation (APA):
Gousiadou, C., Gotfredsen, C. H., Jensen, S. R., & Tsoukalas, M. (2012). Iridoids from *Scutellaria goulimyi* Rech. f., Lamiaceae. Morphological and chemical relations with *Scutellaria albida* L. ssp *albida*. *Biochemical Systematics and Ecology*, 43, 139-141. <https://doi.org/10.1016/j.bse.2012.03.004>

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Iridoids from *Scutellaria goulimy* Rech. f., Lamiaceae. Morphological and chemical relations with *Scutellaria albida* L. ssp *albida*.

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Keywords: *Scutellaria goulimy*; *S. albida* subsp. *albida*; Lamiaceae; iridoid glucosides; chemotaxonomy; agnucastolide B

1. Subject and source

Scutellaria goulimy is a plant of the Lamiaceae family, endemic of the W Aegean island of Evvia (Trigas & Iatrou, 2006). With a chromosome number of 34, it can be found in Northern Evvia at an altitude of 250-700 m, growing equally well on both serpentine and limestone substrate. The influence of serpentines in speciation processes in plants is well known (Kruckeberg 1951, 1954, 1967; Proctor & Woodell 1975). The endemism related to ultramafic substrate on Evvia, exhibits a mixture of evolutionary recent and older taxa, which can be grouped into certain categories with respect to their origin. *S. goulimy* is considered as a neoendemic, whose taxonomic relative, *Scutellaria albida* s. l., has a distribution from N. Italy to Iran. It may be the result of an adaptation of older populations to the special ecological conditions of the ophiolitic substrate. Strong crossing barriers were observed in *S. goulimy* Rech. fil., and, in spite of little morphological differentiation from *S. albida* L. s. str., it is treated as a separate species (Bothmer, 1985). The *S. albida* group is predominantly white flowering, often with purple spots on the lower corolla lip (nectar guidance). (Bothmer, 1991)

Given the close relationship between the two species (Bothmer, 1991), we undertook to investigate chemical similarities between *S. goulimy* and *S. albida* L. ssp *albida* (Gousiadou et al, 2007; unpublished results) for taxonomic purposes. To our knowledge, this is the first report concerning the chemical fingerprint of *S. goulimy*.

The aerial parts of *S. goulimy* were collected at Northern Evvia in June 2010 and a voucher specimen was deposited in the Herbarium (ACA- Gousiadou 010).

2. Previous work

The genus *Scutellaria* is well known for the wide chemical variation within the representative plants (Shang et al, 2010). Due to this diversion, the infrageneric classification is not well understood, although the position of the genus in the Lamiaceae family remains established (Beardsley et al, 2006). Previous investigations in the *S. albida* group (Çalis et al., 1993, Bruno et al., 1996, Skaltsa et al., 1996, Shang et al., 2010) revealed the presence of iridoid glucosides. Iridoids have been used as chemical markers for the Lamiiflorae superorder, and, in chemosystematics, the iridoid character is important in plant classification, phylogeny and evolution (Sampaio-Santos and Kaplan, 2001). In the eastern part of the Mediterranean, the genus has shown to be taxonomically extremely complicated, resulting to much controversy as to delimitation of taxa (Bothmer, 1991).

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3. Present study

Eight iridoid glucosides and a phenylethanoid glucoside were isolated from the aerial parts of *S. goulimyi*, namely 8-*epi*-loganic acid (Damtoft et al., 1984); globularin (Foderaro & Stermitz 1992); 6'-*O-p-E*-coumaroyl-8-*epi*-loganic acid (Gousiadou et al 2007); catalpol, albidoside, scutellarioside II, mussaenosidic acid, (Çalis et al., 1993); agnucastoid B (Ayşe Kuruüzüm-Uz et al, 2003); martynoside (Warashina et al., 1992).

Dry plant material (30 g) was homogenized with ethanol (200 ml) and left to extract for a week. Then it was filtered, taken to dryness and partitioned in H₂O-Et₂O. The aqueous extract was concentrated (1.07 g), dissolved in H₂O and subjected to reversed phase chromatography using as solvent H₂O–MeOH mixtures of decreasing polarity (25:1 to 1:1). Fraction A (25:1) yielded catalpol (30 mg); fraction B (10:1) mussaenosidic acid (25 mg) and 8-*epi*-loganic acid (15 mg); fraction C (2:1) scutellarioside II (12 mg), globularin (19 mg), albidoside (30 mg) and 6'-*O-p-E*-coumaroyl-8-*epi*-loganic acid (6 mg) and finally fraction D (1:1) yielded agnucastoid B (20 mg) and martynoside (10 mg).

4. Chemotaxonomic significance

Thus, the main constituents of *S. goulimyi* are iridoids, as it is the case with *S. albida* ssp *albida*. The two plants have a very similar chemical profile, characterized by the presence of catalpol, mussaenosidic and 8-*epi*-loganic acid and their esters. The presence of catalpol is significant, since it is a useful taxonomic marker for the genus *Scutellaria* (Cole et al, 1991; Paton, 1990b). The isolation of 8-*epi*-loganic acid, occurring biosynthetically from 8-*epi*-deoxy-loganic acid (Damtoft, 1994), is important, since the exact determination of the configuration at C-8 is of considerable taxonomic significance (Jensen et al., 1989; Naas and Rimpler, 1996).

However, there are differences between the two plants. Chemically, *S. goulimyi* is simpler and seems to lack caffeoyl or feruloyl substitution present in *S. albida*. No aglucones or dihydro-derivatives have been isolated. Instead, we observed the presence of agnucastoid B [(6'-*O*-(6,7-dihydrofoliamenthoyl)-mussaenosidic acid] first isolated (Ayşe Kuruüzüm-Uz et al, 2003) from *Vitex agnus-castus* (Verbenaceae). This is the first report of an iridoid glucoside substituted with a foliamenthic acid isolated from Lamiaceae.

Acknowledgments

We thank Dr. Theophanis Constantinidis (Assistant Professor, Faculty of Biology, University of Athens) for the identification of the plant material.

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